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Difference in the behavior of oxygen deficient defects in Ge-doped silica optical fiber preforms under ArF and KrF excimer laser irradiation

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Photobleaching of optical absorption bands in the 5 eV region and the creation of others at higher and lower energy have been examined in the case of ArF (6.4 eV) and KrF (5 eV) excimer laser irradiation of $3GeO_2$:$97SiO_2$ glasses. We report a difference in the transformation process of the neutral oxygen monovacancy and also of the germanium lone pair center (GLPC) into electron trap centers associated with fourfold coordinated Ge ions and Ge-E′ centers when we use one or the other laser. Correlations between absorption bands and electron spin resonance signals were made after different steps of laser irradiation. It was found that the KrF laser generates twice as many Ge-E′ centers as the ArF laser for the same dose of energy delivered. The main reason for this difference is found to be the more efficient bleaching of the GLPC (5.14 eV) by the KrF laser compared to that by the ArF laser.
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I. INTRODUCTION

Defect formation in SiO_2:GeO_2 glasses by illumination with ultraviolet (UV) radiation is now attracting much interest since it is closely related to the photoinduced refractive index change leading to the formation of Bragg gratings[1] and to second harmonic generation.[2,3] A significant photosensitive response of germano-silicate glasses has been linked to the presence of oxygen-deficient germanium point defects in the glass structure and to the photorefractive index change caused by the defects induced by UV absorption.[4–9] These defects are responsible for a strong absorption band at 240 nm (5 eV) due to the Ge oxygen-deficient center (GODC) which is composed of two possible components, the neutral oxygen monovacancy (NOMV) (Ge-Ge, SiGe or Si-Si) (5.06 eV)[4] and the neutral oxygen divacancy (NODV) (Ge^{2+}), also known as the germanium lone pair center (GLPC)[4,10,11] (5.14 eV). The photoconversion of the NOMV component to the germanium electron center (GEC)[6,7,12] which in turn photochemically converts to Ge-E′ centers under prolonged irradiation with ArF or KrF laser has been reported by Nishii *et al.*[13] The generation of GECs is known to be induced by strong UV photon irradiation from a KrF or a XeCl excimer laser through a two-photon process,[6,7] but the structure of the electron donor required to generate the GEC is still debated among different types of GODCs. Hosono *et al.*[14] reported the formation of germanium electron centers in $[SiO_2]_9$ $[GeO_2]$ glasses by irradiation with excimer laser light via two-photon absorption processes for ArF, KrF, and XeCl, but no significant difference in the formation efficiency was seen between ArF and KrF laser light. It was recently shown that the 400 nm (blue) photoluminescence increases with KrF laser irradiation but decreases with ArF.[15] It was also noted by Albert *et al.* that the photoinduced refractive index change of Ge-doped silica is larger with the ArF laser than it is with the KrF laser.[16] In the present research, we have measured the induced absorption and electron spin resonance (ESR) spectra following UV irradiation from KrF (5.0 eV) and ArF (6.4 eV) excimer lasers on different Ge-doped samples cut from the same rod. We find two different conversion processes for the two components [NOMV (5.06 eV) and GLPC (5.14 eV)] of the 5 eV band depending on the photon energy of the lasers used to irradiate the samples. The main goal of this research is to shed light on the processes at the origin of this difference. Good correlation has been found between the measured absorption bands and the concentration of the induced paramagnetic GEC and Ge-E′ defects calculated from their ESR signals.

II. EXPERIMENT

The samples used were optically polished glass plates 0.5 mm thick, cut from a germania-silicate glass rod prepared by the vapor phase axial deposition method. Their nominal chemical composition is $3GeO_2$:$97SiO_2$ in mol %. The optical absorption measurements in the 190–400 nm wavelength range were carried out using a Cary-5 spectrophotometer. The irradiation of the samples was performed by a Lumonics 500 excimer laser operating with 20 ns pulses at 20 Hz with pulse energies at 248 (KrF) and 193 nm (ArF) of 300 and 120 mJ/cm^2, respectively. The ESR studies were

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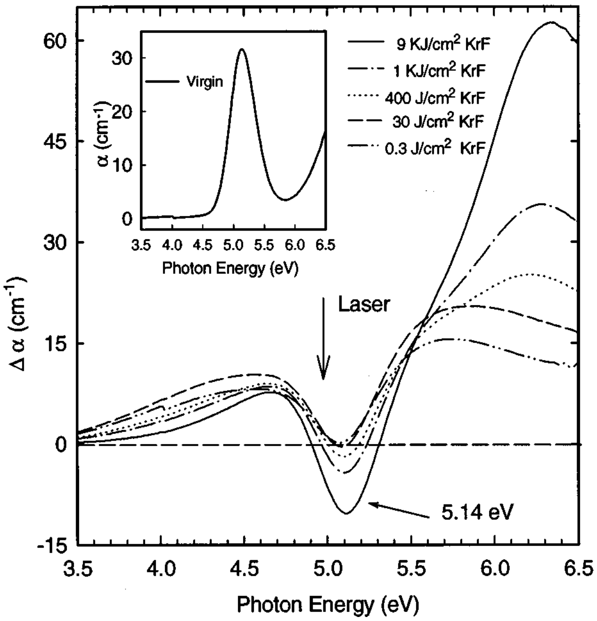

FIG. 1. Change in the optical absorption at different doses of KrF (5.0 eV) irradiation. The dashed line spectrum (30 J/cm^2) is related to the ESR signal of Fig. 4(a). The dotted line spectrum (400 J/cm^2) is related to the ESR signal of Fig. 4(b). The inset is the absorption spectrum of the virgin sample before irradiation.

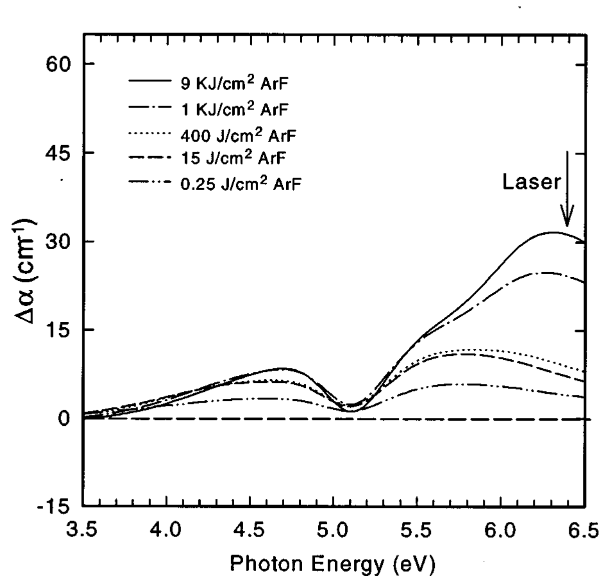

FIG. 2. Change in the optical absorption at different doses of ArF (6.4 eV) irradiation.

made using an X-band Bruker ESP-300E spectrometer to evaluate the presence and development of paramagnetic structural defects in the material. The spin concentrations were determined by double numerical integration of first derivative spectra, and by comparison with the signal from a standard strong pitch of known weight provided by the Bruker company. UV absorption and room temperature ESR spectra were taken after a number of pulses to observe the possible bleaching effects of the UV radiation on the variations of the populations of the paramagnetic and optical centers.

III. RESULTS

The inset of Fig. 1 shows the initial absorption spectrum of the sample, with a strong feature near 5 eV. This 5 eV absorption is characteristic of germanium oxygen-deficient centers and not due to silica point defects which are responsible for near 5 eV absorption bands that are at least two orders of magnitude smaller. Figures 1 and 2 show the difference of the induced absorption coefficient spectra in the UV region obtained after irradiation of the samples at different doses of KrF and ArF radiation, respectively. As can be seen, the first laser pulses in both cases induce strong absorption bands on both sides of the 5 eV band region. Deconvolution of the spectrum representing the induced absorption after a single pulse of KrF laser shows four spectral components of Gaussian shape: two around 4.60 and 5.80 eV are positive and another one near 5.06 eV is negative (see the inset of Fig. 3). A fourth band near 6.4 eV is needed to complete the induced spectrum, indicating that a small Ge-E′ contribution has already occurred (see Table I for the full width at half maximum of each absorption band). At higher fluence (from 400 J/cm^2), the 6.4 eV band increases strongly for both lasers (the deconvolution of the KrF case is shown on Fig. 3).

It has been shown that the 4.5 and 5.8 eV bands are related to GECs[17] which are paramagnetic defects [Ge(1) and Ge(2) in Ref. (17)]. According to Friebele and Griscom[17] Ge(1) and Ge(2) are assigned to two kinds of GECs. Ge(1) is assigned to the GEC of which all of the four next nearest neighbors are silicons, while Ge(2) is assigned to the GEC

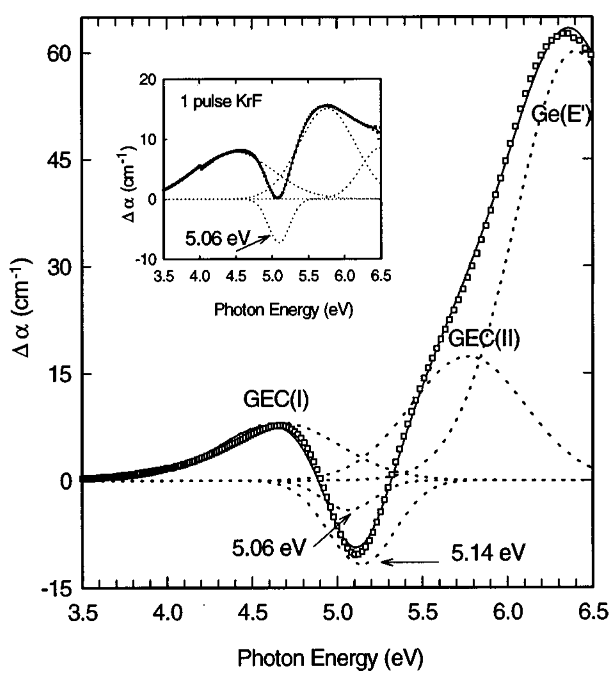

FIG. 3. Deconvolution of the difference absorption spectra of $3GeO_2$:$97SiO_2$ glasses before and after irradiation by 9 kJ/cm^2 KrF. Open squares denote the experimental data, the solid line is the fitted result and the dotted lines are the Gaussians needed for the fit. The inset shows the difference absorption spectra of $3GeO_2$:$97SiO_2$ glasses before and after irradiation of 300 mJ/cm^2 of KrF radiation.

TABLE I. Peak positions and values of the full width at half maximum (FWHM) of the five absorption components used in this study.

Peak position (eV)	FWHM (eV)	Assignment	Reference
4.6	1.3 ± 0.05	GEC(I)	[4.5, Ge(1)] in Ref. 17
5.06	0.38 ± 0.01	NOMV	(4)
5.14	0.48 ± 0.01	GLPC	(4)
5.8	0.79 ± 0.03	GEC(II)	Ge(2) in Ref. 17
6.4	0.87 ± 0.03	Ge-E′	(5)

which has one germanium atom at the next nearest neighbors. The other observed absorption band around 6.4 eV is known to be related to Ge-E′ centers[5] which are also paramagnetic defects. We therefore measured the ESR signals to verify the origin of those bands and to assign them to the observed absorption bands. The ESR measurements on samples irradiated with different doses until a cumulative dose of 30 J/cm^2 of KrF or ArF pulses show only the GEC's signal as can be seen in Fig. 4(a). This dose corresponds to optical spectra that show only the two bands at 4.6 and 5.8 eV positive and one at 5.06 eV negative (dashed line spectra in Figs. 1 and 2). With a UV exposure larger than few hundred J/cm^2, a new absorption band appears at 6.4 eV as well as the ESR signal of the Ge-E′ center. Figure 4(b) shows the ESR signal of both GEC and Ge-E′ centers following irradiation with 1 KJ/cm^2 KrF. A similar signal with lower in-

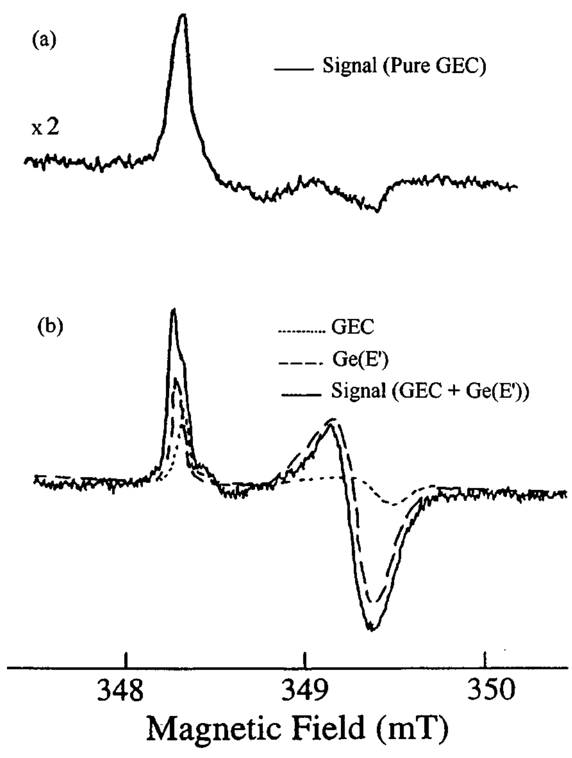

FIG. 4. (a) GEC signal created after irradiation with 30 J/cm^2 KrF, (b) both GEC and Ge-E′ signals after irradiation with 1 kJ/cm^2 KrF. The pure signal of GEC (dotted line) is obtained in Ge-doped silica after gamma-ray irradiation at 77 K (Ref. 12). Pure Ge-E′ (dashed line) can be obtained from Ge-doped silica with UV illumination (Ref. 4).

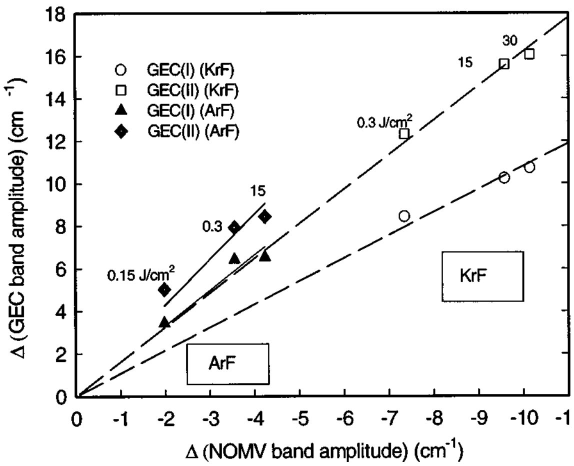

FIG. 5. Correlation between the intensities of the NOMV (5.06 eV) band and the GEC (4.6 and 5.8 eV) bands in the case of ArF and KrF laser irradiation of up to 30 J/cm^2 (solid and dashed lines are the result of the linear regression relation). The labels for each data point refer to the cumulative laser fluence corresponding to that point.

tensity is obtained after the same dose of ArF irradiation. We also notice that the concentration of the GEC saturates within a small dose of one or the other laser irradiation, yet that of the Ge-E′ center increases with increasing irradiation dose (almost the same GEC signal intensity after 30 J/cm^2 and 1 kJ/cm^2 in Fig. 4). It is evident then to assign the first created absorption bands at 4.6 and 5.8 eV to GEC and the last one at 6.4 eV to Ge-E′. After a cumulative dose of 9 kJ/cm^2 from each laser on two different samples, we measured the ESR signal and evaluated the total concentration of the induced GEC and Ge-E′ paramagnetic centers. We find a concentration of 8×10^{18} spins/cm^3 induced by KrF and 4.8×10^{18} spins/cm^3 in the ArF irradiation case, while the deconvoluted amplitude of the 6.4 eV absorption band is 76 cm^{-1} for KrF and 43 cm^{-1} for ArF, thereby confirming a quantitative relationship between the Ge-E′ and the 6.4 eV absorption.

Figures 5, 6 and 7 show the change in color center populations obtained by deconvolution of the absorption spectra

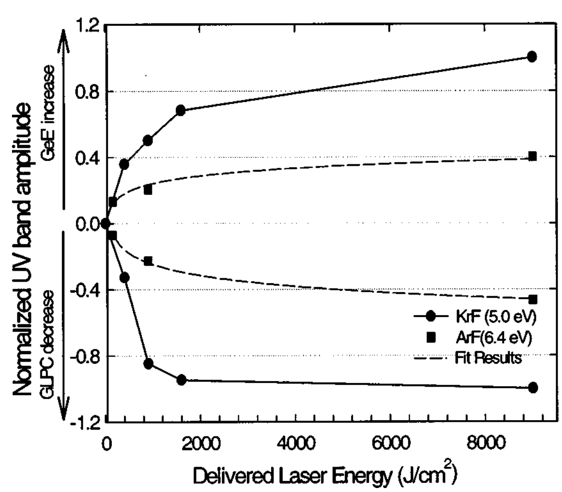

FIG. 6. Evolution of the deconvoluted amplitudes of the GLPC (5.14 eV) and the Ge-E′ (6.4 eV) bands induced by irradiation with KrF (solid lines) and ArF (dashed lines) laser light.

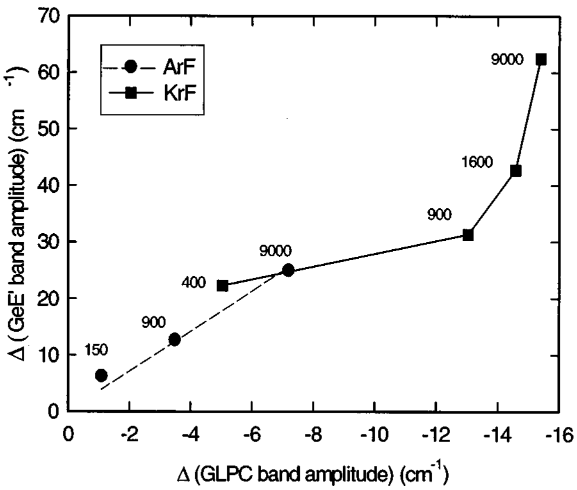

FIG. 7. Correlation between the bleaching of the GLPC (5.14 eV) and the growth of the Ge-E′ (6.4 eV) in the case of ArF irradiation and KrF irradiation. The labels for each data point refer to the cumulative laser fluence (J/cm^2) corresponding to that point.

obtained following irradiation of the samples by different doses of KrF and ArF laser radiation. Two distinct regimes describe the data. In Fig. 5, we see that for small doses of laser irradiation (up to 30 J/cm^2) there is a linear relationship between the bleaching of the NOMV (5.06 eV) band and the growth of the GEC (4.6 and 5.8 eV) bands for both lasers. A linear regression passing through the origin for all the data suggests that there is a one-to-one relationship between the decrease of NOMV and the growth of GECs. However, the speed of this process depends on the wavelength of the laser used. In fact, as shown in the Fig. 5, the conversion process is faster in the case of the KrF irradiation which has a photon energy closer to the energy of the NOMV defect. Also, it is clear that this NOMV to GEC process requires very little laser dose and saturates (see the dose labels in Fig. 5).

At higher fluence of both lasers, a second process dominates. The dotted lines in Figs. 1 and 2 denote the beginning of the growth of the new band around 6.4 eV at a dose of 400 J/cm^2 for both lasers. The new conversion process is shown in Fig. 6 as a relation between the bleaching of the GLPC (5.14 eV) absorption band and the creation of the Ge-E′ (6.4 eV). The data are normalized to the maximum deconvoluted band amplitude (obtained with KrF) for both the GLPC and Ge-E′ bands. We can clearly see the decrease in the intensity of the GLPC and the increase of the intensity of the Ge-E′ at high laser doses. The intensities of the created Ge-E′ band and the bleached GLPC band by the ArF laser (dashed lines) are almost half those of the bands obtained with the KrF laser (solid lines). This difference is also demonstrated by the ESR measurements which give concentrations of Ge-E′ centers following KrF irradiation, almost twice those obtained under ArF irradiation (8×10^{18} vs 4.8×10^{18} spins/cm^3). The correspondence between the optical band amplitudes of the bleached GLPC and the Ge-E′ created is shown in Fig. 7. For the ArF laser, the relationship is again linear with a slope going through the origin, meaning that Ge-E′ are created at the same rate as GLPCs are bleached. However for the KrF laser, the growth of the Ge-E′ depends highly nonlinearly on the bleaching of GLPCs. In particular, at higher fluences the Ge-E′ centers increase rapidly while the changes in GLPCs have saturated. In addition, it takes about 10 times more ArF photons than KrF photons to generate a given amount of Ge-E′ amplitude change.

IV. DISCUSSION

The nonlinear relationship between the generation of Ge-E′ centers and the bleaching of the GLPC band at 5.14 eV can be explained if the following model is used. The UV-induced formation of Ge-E′ centers observed by ESR and optically appears to arise from three separate mechanisms. First there is bleaching of the NOMV to form GECs, possibly through an intermediate stage involving Ge-E′. This process occurs in the initial stage of irradiation with both lasers and also with low intensity UV irradiation from a Xe/Hg discharge lamp.[18] This is likely the origin of the weak photosensitivity observed in the earliest reports on this phenomenon.[1] Then, a second mechanism comes into play in which GLPCs at 5.14 eV are transformed into Ge-E′ centers (6.4 eV absorption and the ESR signature). In the case of UV irradiated H_2 loaded samples, Awazu *et al.* have shown a one-to-one correlation in each concentration between the GLPC reduction and the Ge-E′ center generation.[18] This second process does not occur with low intensity UV light, and is stronger when the irradiation is at the wavelength of the KrF laser than at the wavelength of the ArF laser. The difference is likely due to the fact that the photon energy of the KrF laser is resonant with the peak of the GLPC absorption. Finally, when the GLPC population is exhausted, a third mechanism appears to be the source of a continued growth of Ge-E′ centers at high doses of KrF laser light. This third process is not seen with the ArF laser because the complete bleaching of the GLPCs has not occurred even with 9 kJ/cm^2 of delivered laser fluence.

However, the model does not fully explain the situation since there is only a factor of 2 difference between Ge-E′ generation rates of the two lasers, and it is well known that the photoinduced refractive index change of Ge-doped silica is higher with the ArF laser than it is with the KrF laser.[16] Therefore, (a) there must be a precursor population other than GLPC for Ge-E′ centers in the case of ArF photons and/or (b) photosensitivity is not uniquely determined by Ge-E′ growth. The presence of different precursor populations for photoinduced changes under ArF and KrF laser irradiation was confirmed recently by observing that 400 nm (blue) photoluminescence increases with KrF laser fluence but decreases with ArF laser fluence[15] (for glasses with similar oxygen-deficient germanium point defect absorption bands, referred to as ''low-Ge'' in Ref. 15).

V. CONCLUSIONS

GECs and Ge-E′ paramagnetic centers are created from oxygen-deficient centers by irradiation with ArF or KrF excimer laser light. Three distinct regimes are found to describe the changes in the absorption spectra. First, NOMV (5.06 eV) centers are bleached and GECs (4.6 and 5.8 eV) are created for a cumulative dose of up to 30 J/cm^2 of one or the other lasers. This result is confirmed by the ESR results. Second, at higher fluence of both lasers, new Ge-E′s are created and are associated with bleaching of the GLPCs (5.14 eV). This process is found to be much more efficient for KrF (5 eV) photons than for ArF (6.4 eV) photons. Third, when the GLPC population is exhausted, the growth of the Ge-E′s continues without significant change in the optical absorption bands occurring at lower energies. This last process requires large doses of laser irradiation, doses that are comparable to the ones used in Bragg grating formation in fibers. It is therefore likely that this last process, rather than bleaching of near 5 eV color centers, is responsible for photosensitive refractive index changes of significant magnitude (i.e., greater than 10^{-4}). However, the results presented here on the growth of the Ge-E′ optical band are in distinct contrast with the results of Refs. 16 and 19 in which the refractive index changes obtained in the Ge-doped silica core optical fibers are larger or are obtained faster by irradiation with the ArF laser than the KrF laser. Furthermore, it is now firmly established that in nearly all types of doped silica glasses, the ArF laser is more efficient for the generation of large photoinduced index changes than is the KrF laser.[20] Therefore, the often-assumed link between the growth of the Ge-E′ optical absorption band near 6.4 eV and the induced refractive index changes in fibers and waveguides should be seriously reconsidered.

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[1] K. O. Hill, Y. Fujii, D. C. Johnson, and B. S. Kawazaki, Appl. Phys. Lett. **32**, 647 (1978).
[2] T. E. Tsai, M. A. Saifi, E. J. Friebele, D. L. Griscom, and U. Österberg, Opt. Lett. **14**, 1023 (1989).
[3] K. D. Simmons, S. Larochelle, V. Mizrahi, G. I. Stegeman, and D. L. Griscom, Opt. Lett. **16**, 141 (1991).
[4] H. Hosono, Y. Abe, D. Kinser, R. A. Weeks, K. Muta, and H. Kawazoe, Phys. Rev. B **46**, 11 445 (1992).
[5] H. Hosono, M. Mizuguchi, H. Kawazoe, and J. Nishii, Jpn. J. Appl. Phys., Part 2 **35**, L234 (1996).
[6] J. Nishii, K. Fukumi, H. Yamanaka, K. Kawamura, H. Hosono, and H. Kawazoe, Phys. Rev. B **52**, 1661 (1995).
[7] M. Fujimaki, K. Yagi, Y. Ohki, H. Nishikawa, and K. Awazu, Phys. Rev. B **53**, 9859 (1996).
[8] M. Gallagher and U. Österberg, J. Appl. Phys. **74**, 2771 (1993).
[9] V. B. Neustruev, J. Phys.: Condens. Matter **6**, 6901 (1994).
[10] K. Awazu and H. Kawazoe, J. Appl. Phys. **68**, 2713 (1990).
[11] L. Skuja, J. Non-Cryst. Solids **149**, 77 (1992).
[12] Y. Watanabe, H. Kawazoe, K. Shibuya, and K. Muta, Jpn. J. Appl. Phys., Part 1 **25**, 425 (1986).
[13] J. Nishii, H. Yamanaka, H. Hosono, and H. Kawazoe, Opt. Lett. **20**, 1184 (1995).
[14] H. Hosono, H. Kawazoe, and J. Nishii, Phys. Rev. B **53**, R11 921 (1996).
[15] L. B. Allard, J. Albert, J. L. Brebner, and G. R. Atkins, Opt. Lett. **22**, 819 (1997).
[16] J. Albert, B. Malo, F. Bilodeau, D. C. Johnson, K. O. Hill, Y. Hibino, and M. Kawachi, Opt. Lett. **19**, 387 (1994).
[17] E. J. Friebele and D. L. Griscom, *Defects in Glasses*, edited by F. L. Galeener, D. L. Griscom, and M. J. Weber, Materials Research Society Proceedings Vol. 61 (Materials Research Society, Pittsburgh, 1986), pp. 319–331.
[18] K. Awazu, H. Onuki, and K. Muta, J. Non-Cryst. Solids **211**, 158 (1997).
[19] J. Albert, B. Malo, K. O. Hill, F. Bilodeau, D. C. Johnson, and S. Thériault, Appl. Phys. Lett. **67**, 3529 (1995).
[20] J. Albert, *OSA Technical Digest Series* (Optical Society of America, Washington, 1995), Vol. 22, pp. 229–231, and references therein.